

A DEGRADATION STUDY OF
DISLodgeABLE AZINPHOS-METHYL RESIDUE
ON TOMATO FOLIAGE IN SAN DIEGO COUNTY

by

Keith T. Maddy, Staff Toxicologist
Dennis B. Gibbons, Environmental Hazards Specialist
Steven L. Kilgore, Environmental Hazards Specialist
Linda P. O'Connell, Environmental Hazards Specialist
Nirmal K. Saini, Agricultural Chemist

HS-1224 October 7, 1987

California Department of Food and Agriculture
Division of Pest Management, Environmental
Protection and Worker Safety
Worker Health and Safety Unit
1220 N Street, Sacramento, California 95814

SUMMARY

During November of 1983, a degradation study of dislodgeable azinphos-methyl (Guthion) residue on tomato foliage was conducted in San Diego County. The reentry interval for azinphos-methyl on tomatoes is one day. Samples were collected up to 14 days after the application. Each sample was analyzed for both the parent material (azinphos-methyl) and its oxon. Knaak and Iwata (1982) have calculated residue level values which represent the maximum amount of dislodgeable material which may be present on the foliage that can be present without concern of possible hazard to unprotected workers. These values are 3.0 ug/cm² for the parent (thion) material and 0.05 ug/cm² for the major degradation product (oxon). A residue level of 1.6 ug/cm² has been calculated as the safe level for azinophos-methyl and its oxon combined. None of the sample results taken exceeded this suggested safe level. This study substantiates that under the conditions of this study, the existing reentry interval is adequate.

INTRODUCTION

In June 1971, the California Department of Food and Agriculture established reentry intervals for specific crop/pesticide combinations. A reentry interval is the time period that must elapse between the application of a pesticide and the entry of unprotected workers into the treatment area for contact with treated foliage. This waiting period was instituted to allow sufficient time for toxic materials to environmentally degrade to a low toxicity residue level. The adequacy of some of these reentry intervals has not been evaluated since their introduction. The objective of this study was to monitor the foliar decay rate of azinphos-methyl. This study is one of several studies conducted in 1983 to validate existing safety intervals.

Azinophos-methyl (Guthion) is a non-systemic organophosphate insecticide and acaricide of long persistence (Hayes, 1982). It has an oral LD₅₀ (rat) of 13 mg/kg and a dermal LD₅₀ (rat) of 220 mg/kg (NIOSH, 1983).

Knaak and Iwata have calculated residue levels considered safe for azinophos-methyl and its oxon. These values are 3.0 ug/cm² for the parent (thion) material and 0.05 ug/cm² for the major degradation product (oxon). These residue level values represent the maximum amount of residue material that can be present on foliage without concern of possible hazard to unprotected workers. A residue level of 1.6 ug/cm² has been calculated as the safe level for azinophos-methyl and its oxon combined. This study investigated the rate at which the residue levels declined to levels considered to be of low hazard.

METHODS

With assistance from the San Diego County Agricultural Commissioner's staff, a local tomato grower was contacted and asked to cooperate in this study. One tomato field was monitored for 14 days after the azinphos-methyl application. The application rate was 1.5 lbs. (0.75 lbs. a.i.) of Guthion 50W per acre.

The tomato field was divided into three areas. One row from each area was selected and identified with markers for sampling. Twenty plants in each row were chosen for sampling. Three replicate samples were taken from each plant each sampling day. Each composite sample consisted of 60 leaf disks, one leaf disk from each of the 60 plants. These samples were collected using a 2.54 cm disk leaf punch which was cleaned with alcohol between samples. They were collected approximately 24 and 48 hours after the application, then again on the sixth, seventh, thirteenth and fourteenth day after the application.

The leaf sample bottles were sealed with aluminum foil, capped, and stored on ice. Samples were shipped to Chemistry Laboratory Services in Sacramento for analysis. Dislodgeable residue was removed by mechanically shaking the leaf disks with a water-surfactant solution. The aqueous wash was extracted with ethyl acetate, dried with anhydrous sodium sulfate, and concentrated or diluted as necessary. The analysis was by gas chromatography.

RESULTS

The analytical results for each composite sample as well as a calculated average for each day are presented in Table 1. The minimum detectable level (0.003 ug/cm^2) was used in calculating the averages for each azinphos-methyl oxon sample under the detection limit. None of the azinphos-methyl samples were below the minimum detectable level of 0.0002 ug/cm^2 . Table 2 shows the maximum and minimum air temperatures as well as the average dew points and wind speeds for the period during which the study was conducted. Table 3 shows the average daily concentrations of selected air pollutants, monitored at a nearby Air Resources Board station in the South Coast Air Basin for the same period. Figures 1 and 2 shows the degradation of azinphos-methyl and its oxon over the fifteen day sampling period.

DISCUSSION

Guthion dislodgeable residue levels have been found to increase for a time after application before decreasing (Maddy, Fong and Cooper, 1985; Maddy et al., 1986). The current study follows a similar pattern with the highest average levels of both azinophos-methyl and its oxon occurred at 48 hours post application. These levels were 1.11 ug/cm^2 and 0.007 ug/cm^2 , respectively. Under the conditions of this study, the sample results never exceeded the recommended (upper limit) safe level of 1.6 ug/cm^2 suggested by Knaak and Iwata (1982). Several factors, such as ambient and radiant temperature, humidity, and solar radiation may influence the degradation of pesticides. These factors were not within the scope of this study to measure and were not taken into account.

Growers usually do not apply maximum rates in an attempt to minimize cost and pest resistance to the pesticide. However, existing safety intervals were established based upon the degradation of maximum label application rates. (The application rate used during this study was one-half the maximum allowable rate recommended by the label.) For purposes of estimating the dislodgeable azinophos-methyl residues for a maximum rate application doubling the highest residue levels gives 2.22 ug/cm^2 azinophos-methyl and 0.014 ug/cm^2 oxon. In this situation, the maximum foliar level that can be present without concern of possible hazard to unprotected workers is exceeded at the expiration of the reentry interval.

REFERENCES

1. Hayes, Jr., M.D., Ph.D. 1982. Pesticides Studied in Man. Williams and Wilkins. Baltimore, pp. 358.
2. Knaak, James B. Minimizing Occupational Exposure to Pesticides: Techniques for Establishing Safe Levels of Foliar Residues. Residue Review, Volume 75.
3. Knaak, J.B. and Y. Iwata. 1982. The Safe Level Concept and the Rapid Field Method - A New Approach to Solving the Reentry Problem.
4. Maddy, K.T., H.R. Fong and C. Cooper. 1985. A Study to Establish a Degradation Profile for Azinphosmethyl (Guthion) on Apple Foliage in Kern County During July 1984.
5. Maddy, K.T., D. Meinders, S. Margetich, S. Saiz and T. Mann. 1986. A Profile of the Degradation of Dislodgeable Foliar Residue After Serial Azinphosmethyl (Guthion) Applications to Peaches; Stanislaus County, 1985.
6. NIOSH. 1983. Registry of Toxic Effects of Chemical Substances. Volume 3. p. 144.

TABLE 1

Days Post Application	A		B		C		Average Azinophos-methyl Level (ug/cm ²)	Average ^{a/} Oxon Level (ug/cm ²)
	Azinophos-methyl (ug/cm ²)	Oxon (ug/cm ²)	Azinophos-methyl (ug/cm ²)	Oxon (ug/cm ²)	Azinophos-methyl (ug/cm ²)	Oxon (ug/cm ²)		
1	1.00	0.007	0.42	0.003	0.67	ND ^{b/}	0.697	0.004
2	1.12	0.007	1.10	0.007	1.11	0.006	1.111	0.007
6	0.73	0.006	0.50	0.006	0.65	0.006	0.627	0.006
7	0.49	0.004	0.57	ND	0.63	ND	0.563	0.003
13	0.014	ND	0.028	ND	0.025	ND	0.022	0.003
14	0.02	ND	0.009	ND	0.01	ND	0.013	0.003

^{a/}Calculations for averages were based on nondetectable levels of azinphos-methyl oxon equivalent to 0.003 ug/cm².

^{b/}ND - indicates none detected; the minimum detectable level for azinphos-methyl was 0.002 ug/cm²; the minimum detectable level for azinphos-methyl oxon was 0.003 ug/cm².

TABLE 2

Temperature (°F)

Date		Maximum	Minimum	Average Dew Point	Average Win Velocity Knots
November	3	83	51	60	SSW6
	4	81	51	61	SW7
	7	75	53	61	SW8
	8	78	59	60	SW5
	9	79	43	53	SW7
	10	51	47	53	SW7
	14	71	54	59	SW8
	15	77	45	56	SW6
	16	72	48	57	SSW7

TABLE 3

Average Concentrations of Selected
Air Pollutants in the South Coast Air Basin
Reported by the Costa Mesa-Placentia Station

Date		Carbon Monoxide (ppm)	Sulfur Dioxide (ppb)	Nitric Oxide (ppb)	Nitrogen Dioxide (ppb)	Oxides of Nitrogen (ppb)	Ozone (ppb)
Nov.	2	2.1	2	88	40	128	9
	3	3.5	7	98	72	163	27
	4	2.0	3	46	46	92	41
	5	0.4	0	8	20	28	27
	6	1.0	0	8	34	42	39
	7	1.5	0	8	47	54	35
	8	1.6	2	20	49	70	30
	9	2.7	7	57	68	124	36
	10	2.3	2	34	63	97	29
	11	0.5	0	0	23	23	19
	12	0.5	0	9	20	29	10
	13	1.1	3	40	22	62	15
	14	1.8	3	37	40	77	16
	15	3.1	10	78	70	148	25
	16	2.5	7	61	50	111	14